電気材料技術雑誌 第14巻第2号
J.Soc.Elect.Mat.Eng. Vol.14, No.2, 2005

PICOSECOND TIME-RESOLVED STUDY OF INTERMEDIATE SPECIES PRECEDING FREE CHARGE CARRIER FORMATION

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Below one can see a survey of the works made during the stays of Eugeny Frankevich at the Yoshino lab. The technique based on the action of pairs of correlated light pulses with a controlled delay time Δt between them was applied for studying second order processes responsible for formation of free charge carriers in conjugated polymers [1-5]. We worked with poly(2,5-dioctyloxy-*p*-phenylenevinylene) and substituted polythiophene, have performed time-resolved experiments within the picosecond time domain, and have got direct evidence on existence of intermediate states preceding free charge carriers at the photo excitation of conjugated polymers. Short lifetime of species involved in the processes permitted to speculate that those are primarily formed excitons and polaron pairs, main part of them being generated without any delay at the absorption of the light.

The technique permits to obtain evidence on the very existence and properties of intermediate active species that work at any intensity of excitation being precursors of the final products not only of the second- but also of the first-order processes.

Short laser pulses irradiate a sample equipped with electrodes. The pulses are arranged in pairs with a controlled delay time Δt between the pulses. Such pairs are repeated continuously with the repetition rate of 1 kHz and an average photocurrent through the sample is measured.

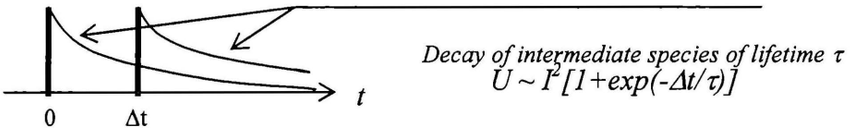
Although the total intensity of the pairs of laser pulses remains the same at any delay time, the yield of second-order products depend on the density of species taking part in the processes. The density of the excited species depends on the superposition of the species produced by the first pulse of a pair and surviving up to the moment of the action of the second pulse. In our case, the products are free charge carriers, and the rate of their formation U depends on the delay time Δt and the intensity of the light I of the two equal pulses as

$$U \propto I^2\left[1 + f(\Delta t)\right] \tag{1}$$

Here $f(\Delta t)$ is a function normalized to unity and describing the decay of species taking part in a second-order process. This formula appears as a result of the integration of the products of a bimolecular reaction between intermediate species generated by two correlated pulses of intensities I_1 and I_2, the second one being delayed by Δt in respect to the first one. In the case of $f(\Delta t)$ having an exponential view with k_1 as a monomolecular decay rate constant, the integration looks like as follows.

$$U \propto \int_0^{\Delta t}\left(I_1 e^{-k_1 t}\right)^2 dt + \int_{\Delta t}^{\infty}\left(I_2 e^{-k_1 (t-\Delta t)} + I_1 e^{-k_1 t}\right)^2 dt = I_1^{\,2} + I_2^{\,2} + 2 I_1 I_2 e^{-k_1 \Delta t}. \tag{2}$$

Average photoconductivity was measured at excitation of the sample by pairs of 150 fs laser pulses of 400 nm wavelength at 1 kHz repetition rate as a measure of the yield U of free charge carriers. The next scheme shows the principle of the technique. Superposition of intermediate species formed under the action of the first and delayed laser pulses of an intensity I makes the yield U of the second order processes dependent on Δt.



An effect on the value of U of the electrical field applied to a sample have permitted to get evidence on involvement of polaron pairs into the recombination process [7, 8]. It is shown that at high enough excitation power (>25 μJ/cm^2 per a pulse) free charge carriers appear as a result of recombination of primarily formed polaron pairs. That process competes with the process of electrical field induced dissociation of polaron pairs. Secondary polaron pairs are shown to be produced in the recombination process, and these pairs, having higher inter-charge distances, dissociate into free charge carriers with a high probability. It was revealed that in substituted polythiophene primary polaron pairs are formed with two distinct inter-charge distances, of about 4 and 10 nm, and relative amounts of the pairs were determined (about 0.9 and 0.1, respectively). We have carried out time-resolved measurements of photoluminescence and photocurrent in poly(3-oktylthiophene) (PAT8) doped with fullerene C_{60}.[6] For photocurrent study we applied a laser two-correlated-pulses technique, which permitted to select electronic processes connected with recombination of intermediate short-living species responsible for formation of free charge carriers. The wavelength and pulse width of the laser pulses were 400 nm and 150 fs, respectively, and delay time (Δt) between correlated pulses was controlled within the ps time domain. It was shown that the average photocurrent in undoped samples has a prominent component originated from inter-pair recombination of polaron pairs. This component, however, changed with doping: at low doping (C_{60} less than 0.1 mol%) it increases, but at higher doping (C_{60} up to 0.5 mol%) it disappears. It is shown that the electron transfer from π-conjugated segments of PAT8 to C_{60} takes about 10 ps, and leads to the formation of polaron pairs, which dissociate into free charge carriers much faster (lifetime is much shorter than 3 ps) than the pairs formed without doping.

Kinetics of decay of polaron pairs as precursors of free charge carriers at photoexcitation of poly(3-octylthiphene) films was observed directly within a picosecond time domain by using the two-correlated-pulses laser technique. Experiments showed that polaron pairs were generated without any noticeable delay after the light absorption. Two kinds of polaron pairs with lifetimes about $\tau_1 \approx 10$ ps, and $\tau_2 \approx 200$ ps were revealed, the lifetimes having been temperature independent in zero electrical field. The value of τ_2 was shown to decrease in a higher electrical field reaching about 30 ps at $E = 10^5$ V/cm. Free charge carriers appear as a result of the pair dissociation.

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